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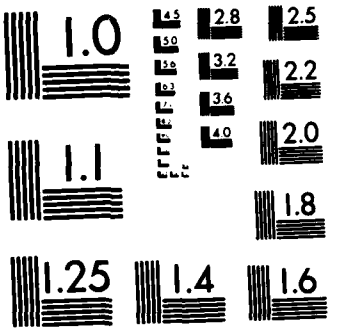

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Research on the development of new photoinitiator systems for spatially selective photochemical machining with lasers has continued smoothly and is progressing well. The porphyrin systems developed during the second quarter continue to look particularly promising. Further experiments on the 2-component photoinitiator systems comprised of 9,10-dibromoanthracene and naphthalene sulfonyl chloride have confirmed that photopolymerization can be selectively enhanced by 2-beam irradiation. This is the first report of a 2-photon, 2-component polymerization system, to our knowledge.

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FOURTH QUARTERLY R AND D STATUS REPORT

on

THREE-DIMENSIONAL PHOTOCHEMICAL MACHINING WITH LASERS

to

AIR FORCE OFFICE OF SCIENTIFIC RESEARCH

from

BATTELLE
Columbus Laboratories
505 King Avenue
Columbus, Ohio 43201

November 30, 1983

Sponsored by

Advanced Research Projects Agency (DOD)
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Monitored by AFOSR Under Contract No. F49620-82-C-0077

Effective Date of contract: June 1, 1982
Contract Expiration Date: May 31, 1984
Amount of Contract Dollars: $270,048, including fee
($196,298 obligated to date)

Principal Investigator/Program Manager: Dr. Robert E. Schwerzel
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FOURTH QUARTERLY R AND D STATUS REPORT

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INTRODUCTION

This document represents Battelle's Fourth Quarterly R and D Status Report to the Air Force Office of Scientific Research on Three-Dimensional Photochemical Machining With Lasers, under Contract No. F49620-82-C-0077, for the period May 1, 1983 through July 31, 1983. (Please note that, although the contract effective date is June 1, 1982, delays in the receipt of a signed contract resulted in an actual start date of August 1, 1982 for the research effort; thus, this report covers the fourth quarter of the actual research effort, as provided in the description of reporting periods in the subject contract.)

Our research efforts during this reporting period have focused on (a) continuing to investigate and characterize the brominated protoporphyrin photoinitiator system we discovered during the second quarter's research, (b) continuing our search for other candidate materials which offer the promise of providing selective photopolymerization when irradiated simultaneously with two laser beams of different colors, but of being inert to the presence of either beam alone, and (c) conducting a detailed

study of a novel 2-component photoinitiator system consisting of 9,10-dibromoanthracene (DBA) and the known photoinitiator, naphthalene sulfonyl chloride (NSC), dissolved in methyl methacrylate. We find that when this system is irradiated with light filtered to excite only the DBA (which absorbs at longer wavelengths than does NSC) relatively little polymerization occurs; however, when a second beam of light, filtered so as to transmit only near-IR wavelengths not directly absorbed by either NSC or DBA, is added the rate of polymerization increases dramatically. This can be explained by assuming that the second beam serves to drive triplet--triplet excitation of DBA. The lowest triplet state of DBA (T_1) is energetically below the T_1 state of NSC, so essentially no excitation of the NSC initiator should be possible with beam 1 alone. The photon energy of beam 2, however, is adequate to excite DBA from T_1 to T_2, which lies above the T_1 state of NSC in energy. Thus, energy transfer can occur from DBA (T_2) to NSC (T_1), leading to efficient photoinitiation from the T_1 state of NSC. To our knowledge, this is the first description of a 2-beam, 2-component photoinitiation system. Such a system may have real advantages fro PCM applications, as it permits one to "uncouple" the optical absorption characteristics of the sample from the concentration of photoinitiator used.

No major items of experimental or special equipment were purchased or constructed during this reporting period, and no program personnel changes occurred. Two project-related trips were made during this reporting period, both by the Principal Investigator, Dr. R. E. Schwerzel. A program review trip was made to Washington, D.C. in May to review results with both DARPA and AFOSR program managers, and a scientific trip was made to Andover, N.H. in July to attend the 1983 Gordon Conference on Organic Photochemistry (where there were major lectures on photoresist technology and photopolymerization). No major problems or deviations from the program plan have been encountered to date.

Fiscal Status:

Amount currently provided for the contract: $196,298
Expenditures and commitments to date (4/30/83): $129,004
Estimated funds required to complete the work: $270,048
Estimated date of completion of work: June 30, 1984

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